

THE COALESCENCE OF HEXAGONAL AND CUBIC POLYMORPHS IN TETRAHEDRAL STRUCTURES AS ILLUSTRATED BY SOME WURTZITE- SPHALERITE CRYSTAL GROUPS*

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ABSTRACT

The structural similarities of the hexagonal and cubic polymorphs of zinc sulfide are illustrated by some unusual wurtzite-sphalerite crystal groups synthesized at this laboratory. In general these crystal groups consist of oriented overgrowths of wurtzite prisms extending from the tetrahedral faces of sphalerite nuclei. The method and theory of their growth is discussed. The coalescence of hexagonal and cubic polymorphs in other tetrahedral structures is reviewed.

INTRODUCTION

The relationship of the crystal structures of wurtzite and sphalerite has been known for some time. This relationship, first described by Bragg (1920), resembles that between cubic and hexagonal close packing. In sphalerite the zinc atoms are on a face-centered cubic lattice, whereas in wurtzite they are nearly in the position of hexagonal close packing. In both structures four sulfur atoms surround each zinc atom tetrahedrally. That the wurtzite structure can be derived from the sphalerite structure simply by rotating every other layer of atoms in sphalerite 180° (60°) around its trigonal axis [111] has been pointed out by Aminoff and Broomé (1931).

In Fig. 1, portion *ABCD* is a 110 cross section through the sphalerite structure while *AEFB* is a 11·0 cross section through the wurtzite structure. *SRHP* and *WURA* outline the unit cells of these substances. As a result of the twinning process, which takes place by a 180° rotation of every other layer of atoms (represented in Fig. 1 by the lines parallel to *AB*), the sphalerite [111] becomes the wurtzite *c* axis. From this twinning relationship wurtzite can be considered as a special form of sphalerite and might be called a polymorphic twin of sphalerite.

MORPHOLOGICAL DESCRIPTION OF SOME ZINC SULFIDE CRYSTAL GROUPS

Recently at this laboratory some crystal groups of zinc sulfide were grown which emphasize the structural relationship of these two poly-

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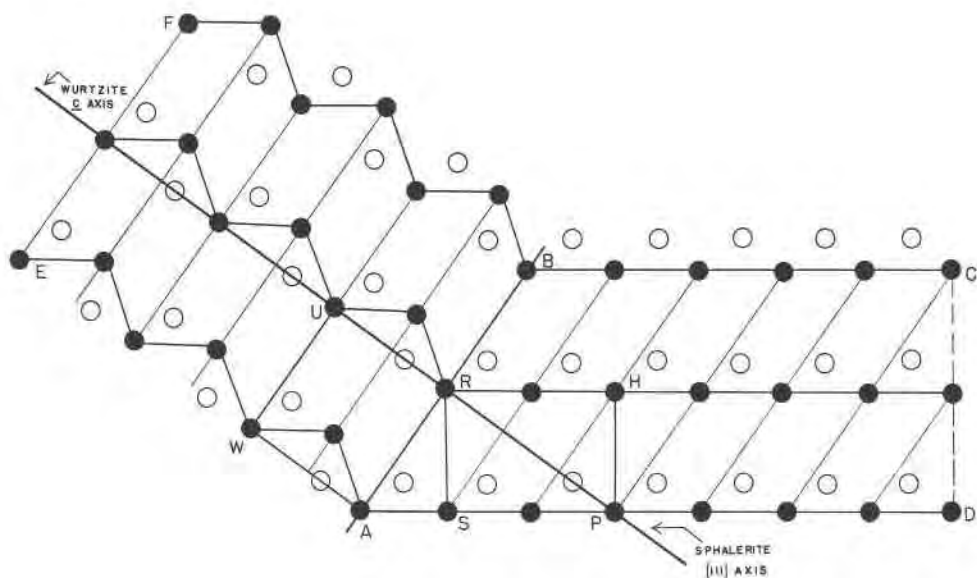


FIG. 1. The twinning relationship of the structures of sphalerite and wurtzite as shown by a 110 section of sphalerite ($ABCD$) and 11.0 section of wurtzite ($AEFB$). Dots represent Zn (or S) and circles represent S (or Zn) atoms.

morphs. These crystal groups, consisting of wurtzite prisms extending from the faces of sphalerite tetrahedrons, can be divided into three main types based upon the position of the wurtzite prisms in relationship to

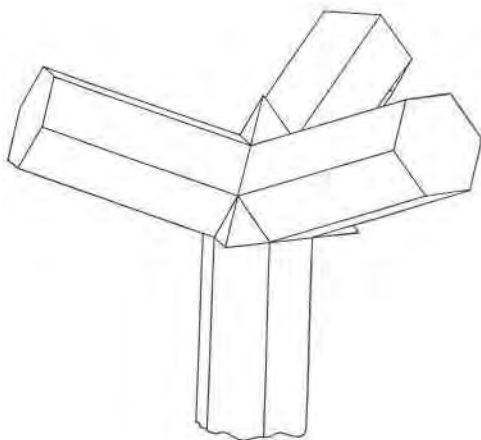


FIG. 2. Idealized drawing of simplest combination of wurtzite-sphalerite groups, showing wurtzite prisms extending from the positive tetrahedral faces of sphalerite.

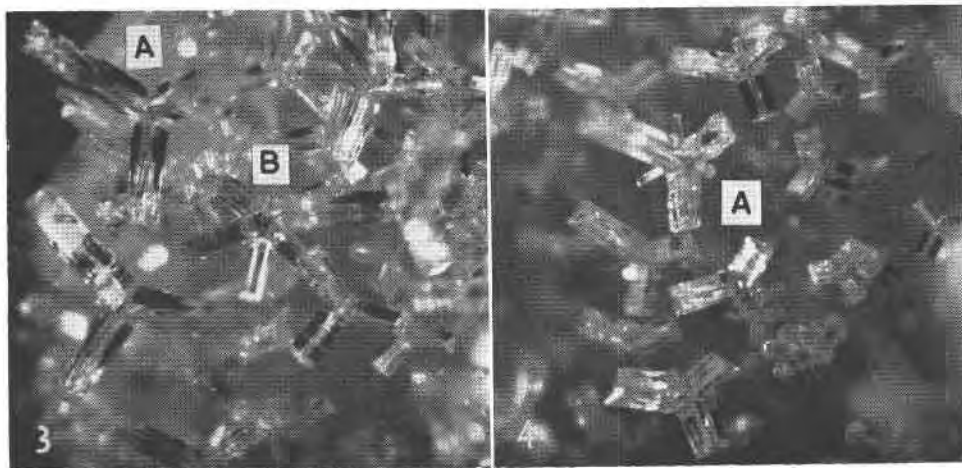


FIG. 3. Photomicrograph of wurtzite-sphalerite groups ($\times 80$). (a) Simplest combination showing wurtzite prisms extending from positive tetrahedral faces. (b) Complex group showing wurtzite prisms growing from positive tetrahedral faces of twinned sphalerite.

FIG. 4. Photomicrograph of crystal groups ($\times 80$). (a) Wurtzite prisms extend from both the positive and negative tetrahedral faces.

the sphalerite nucleus. The simplest combination (Figs. 2 and 3a) consists of four wurtzite prisms extending perpendicular to four faces of a simple sphalerite tetrahedron. The second type (Fig. 4a) is made up of eight wurtzite prisms, four of which protrude from the positive* tetrahedral faces and four from the negative tetrahedral faces of sphalerite. The third, a more complicated type (Figs. 5 and 3b), is composed of wurtzite prisms extending from the positive tetrahedral faces of sphalerite which is itself twinned on $[111]$ by a rotation of 180° . As can be seen in Fig. 5, the twinning axis of the tetrahedron is parallel to the c axis of the vertical wurtzite prism. Looking down the crystal group along this twin axis, one sees six prisms radiating from the tetrahedron 60° apart. Three of these, which are 120° apart, extend out of the positive tetrahedral faces of the lower part of the twin. The other three, also 120° apart, but lying in the intermediate positions, extend from the positive tetrahedron of the upper part of the twin. Wurtzite prisms were not found protruding from the negative tetrahedral faces of the sphalerite twin, but the writers see no reason why this combination is not possible.

In each of the crystal groups mentioned above, the a axes of the wurtzite prisms are parallel to the edges formed by the intersections of the faces of the tetrahedrons. In addition to larger first order prisms, smaller

* The larger faces were considered to be positive.

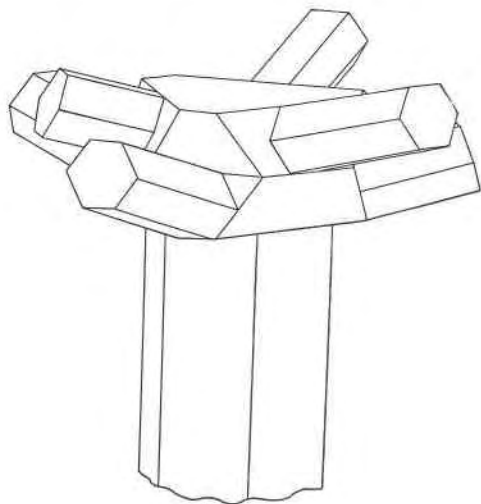


FIG. 5. Idealized drawing of a complex wurtzite-sphalerite group showing wurtzite prisms extending from positive tetrahedral faces of twinned sphalerite. (See Fig. 3*b*.)

second order prisms as well as basal pinacoids are present. Most of the wurtzite prisms are somewhat triangular in shape. This is probably a result of the fact that the prisms are, in a sense, extensions of the original triangular tetrahedral faces. No pyramidal faces were observed. Only rarely could the tetrahedron nuclei be seen.

Because of the well-developed nature of the basal pinacoids and prism faces, the spatial relationships within these groups were readily determined with the use of the optical goniometer. The angular values between the basal pinacoids of the prisms are equal to the angles between the tetrahedral faces of the isometric system ($70^{\circ} 32'$).

X-ray rotation photographs proved the coexistence of wurtzite* and sphalerite. The fact that all the hexagonal prisms *x*-rayed show excellent birefringence indicates that the cubic form exists only in the nucleus of the crystal group.

Figure 6 is a cross section of the crystal group shown in Fig. 2. The section is parallel to the plane formed by the *c* axes of any two of the prisms. The relationship of this to Fig. 1 is clearly seen. Portions *A E F B* and *D H G C* are $11 \cdot 0$ planes through the wurtzite structure, while *A B C D*

* The *x*-ray data indicate that the wurtzite prisms are composed primarily of the $2H$ polymorph (Ramsdell nomenclature, 1947). Some crystals also show evidence of the existence of other polytypes with a higher number of layers. Müller (1952) has shown that these can coexist. As yet no intensive investigation of these forms has been carried on in connection with the crystal groups.

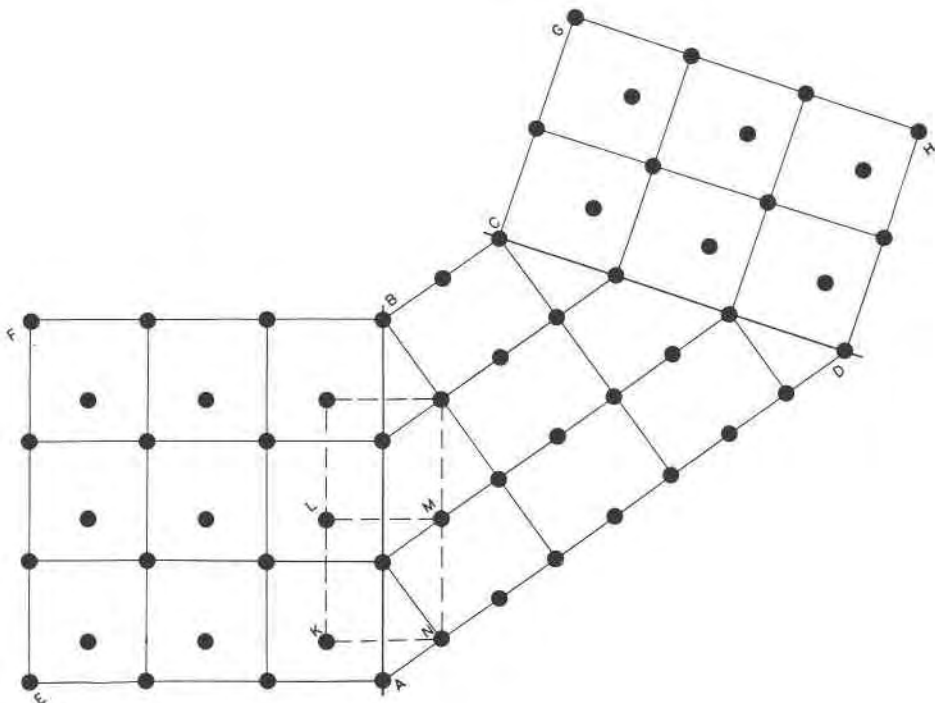


FIG. 6. Cross section of a simple wurtzite-sphalerite group parallel to the plane formed by the c axes of any two prisms. Only the Zn (or S) atoms are designated.

is the 110 plane through the sphalerite structure. Lines AB and CD represent twinning boundaries. The unit cell outlined by $KLMN$ represents a second choice for the wurtzite unit cell which exists partially above and partially below the twinning boundary.

The investigators have encountered much difficulty in finding a name which adequately describes the crystal groups. They have hesitated to call them *twins* because the geometrical relationships involved are based upon two crystal systems. Moreover, the term *polymorphic twin* does not describe them. As was pointed out earlier in this paper, wurtzite is a polymorphic twin of sphalerite because of its similar structure, but this term does not indicate that both structures coexist in an individual unit. A single wurtzite prism can be considered a polymorphic twin of sphalerite. In reality the wurtzite prisms are *oriented overgrowths*, but calling them only this does not adequately bring out the structural and chemical similarity that exists between the two forms. The writers believe that the term *oriented polymorphic twin overgrowth*, which is a combination of these above names would adequately describe the crystal groups.

METHOD OF PREPARATION OF THE ZINC SULFIDE CRYSTALS

The crystals were made by a method described by Lorenz (1891) in which hydrogen sulfide is allowed to react with zinc vapor. A porcelain boat containing 30 mesh granular C.P. metallic zinc was placed in a hydrogen sulfide-filled Vycor U-tube which was preheated to 900° C. Hydrogen sulfide was passed over the boat at this temperature for six hours, a period of time arbitrarily chosen for this experiment. At the end of this period the U-tube was quickly removed and allowed to cool. The hydrogen sulfide atmosphere was maintained during the cooling.

GENERAL APPEARANCE AND PHYSICAL PROPERTIES OF THE CRYSTALS

The zinc sulfide crystals covered the boat, as well as the walls of the portion of the tube surrounding the boat. Masses of the wurtzite-sphalerite groups occurred as segregations in the midst of simple hexagonal wurtzite prisms and fine crystalline masses. No detailed investigation of these latter types has been undertaken. The individual wurtzite-sphalerite groups in these segregated masses are attached perpendicularly to a groundmass by a vertical hexagonal prism which acts as a stem as shown in Figs. 2 and 5. Generally the stem, which may be up to one millimeter in length, is much longer than the other hexagonal prisms which also may vary in length. The crystals are colorless. Under ultraviolet radiation they exhibit strong light blue fluorescence and phosphorescence.

A DISCUSSION OF THE GROWTH OF THE WURTZITE-SPHALERITE GROUPS

It was mentioned above that a hexagonal prism acts as a stem by which the wurtzite-sphalerite group is attached to the groundmass. From this fact it seems logical to conclude that the stem grew first. Next the tetrahedron developed on top of this stem. Finally prisms proceeded to grow out from the remaining three faces of the tetrahedron. No doubt the factors which controlled this growth sequence are numerous. Probably one of the most important factors was a variation in temperature. Müller (1952), who has done considerable work on the tempering of wurtzite crystals at different temperatures, found that hexagonal zinc sulfide transforms completely to the cubic modification when tempered below 870° C. Tempering in the range 870–905° for 10 hours produces a coexistence of cubic and the hexagonal types $2H$, $4H$, $6H$, and $15R$. Type $2H$ predominates at all temperatures above 905°. From these results it appears that temperatures in the neighborhood of 870° are of special importance in determining if zinc sulfide will crystallize in the cubic or hexagonal system. The temperatures in the Vycor tube probably dropped below 870° during the process of crystal growth, thus producing

sphalerite tetrahedrons on top of the primary wurtzite prisms. When higher temperatures were re-established, wurtzite formed on the sphalerite faces. The temperature variation may be attributed to a variation in the flow of the unheated hydrogen sulfide that was passed into the tube during crystal growth or to lack of delicate controls on the muffle furnace.

The significance of the time element is not known. In succeeding experiments simple hexagonal prisms were grown in as short a time as 15 minutes.

So far the writers have been unable to duplicate the results of this experiment. This suggests that the conditions for the formation of this peculiar type of coalescence are very critical.

OTHER INTERGROWTHS OF SPHALERITE AND WURTZITE

Another type of coalescence of sphalerite and wurtzite was produced at this laboratory which consists of isotropic layers or knobs of sphalerite in what appears otherwise to be a continuous hexagonal wurtzite prism (Fig. 7). It can be seen in Fig. 6 that the wurtzite prisms of the crystal groups described in the previous section were formed by twinning along different sphalerite [111] axes, producing two hexagonal units whose c axes are related to each other by an angle of $70^{\circ} 32'$. However, it is also possible for the twinning to occur along the same sphalerite [111] axis

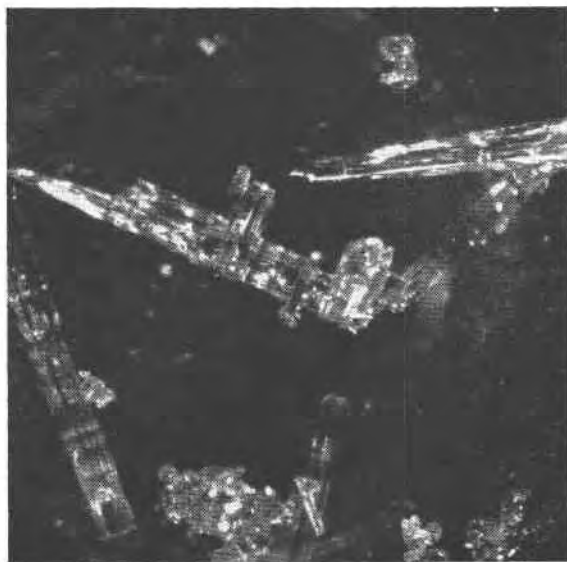


FIG. 7. Photomicrograph of wurtzite prism interrupted by layers or knobs of sphalerite ($\times 92$).

extending from opposite sides of a cubic unit. In this case the two hexagonal prisms would be parallel to a common line, and would have a layer of sphalerite separating them. If the conditions changed a number of times during growth, many cubic layers may develop in what appears to be a continuous hexagonal prism. These crystals were grown in the same manner as those first described in this paper, except that the hydrogen sulfide was passed over the boat at 900° for 12 hours.

The coexistence of sphalerite and wurtzite in nature is well known from schalenblende, which consists of an intimate intergrowth of the two forms. The crystallographic relationships of the two modifications are not well known in this association.

Natural sphalerite is frequently found in multiple contact twins and in complicated lamellar intergrowths. In a special sense a sphalerite twin might be considered as having the wurtzite arrangement in the twin boundary. The twin boundary would be a wurtzite crystal two layers high ($2H$)* in the direction of its c axis ([111] axis of sphalerite). In other words the wurtzite crystal would be one unit cell high and would extend almost indefinitely in its other directions. This is clearly seen in Fig. 8 where $ABCD$ and $AEFB$ are two portions of sphalerite connected by the twinning boundary AB . $FK'N'M$ outlines a portion of the "two dimensional" wurtzite crystal existing at the twin boundary. Multiple contact twins would contain many of these hexagonal levels. Slawson and Kohn (1950) have suggested that the anomalous double refraction commonly observed in cubic zinc sulfide is due to twinning, since the twinning introduces a distortion at the twinning boundary in the otherwise optically isotropic cubic structure.

SIMILAR COALESCENCE AS EXHIBITED IN RELATED SUBSTANCES

Aminoff and Broomé (1936) performed an experiment directly related to the present discussion. They heated crystallized sphalerite in air until it was covered by a thin film of zinc oxide. The resulting film was studied by electron diffraction. It had the hexagonal zinc oxide structure, which is the same as that of wurtzite, and it was so oriented that the c axis was perpendicular to the sphalerite (111) and the a axes were parallel to the

* The wurtzite layer at the twin boundary would generally be considered as being two layers high because this is the common wurtzite structure. However, with the discovery of wurtzite types $4H$ and $6H$ (Fron del and Palache, 1948, 1950), one might consider that these exist at the twin boundary. In Fig. 8 $OPRQ$ outlines a $4H$ unit cell while $STVU$ outlines $6H$. The twin boundary might also be considered to represent the "two dimensional" wurtzite types $8H$ ($WXZY$), $10H$, $12H$, \dots , $2nH$. As a matter of fact a sphalerite twin with exactly n layers on each side of the twin boundary would be a hexagonal polymorph $2nH$ one unit cell high. One could easily see this c_0 dimension macroscopically if n were sufficiently large.

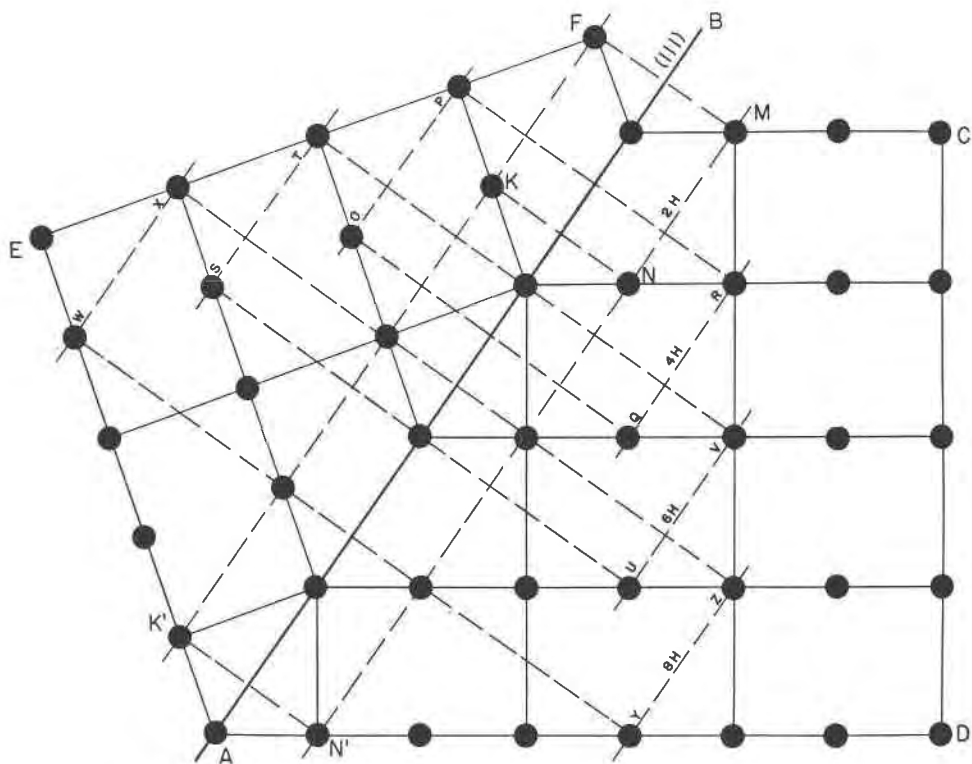


FIG. 8. 110 cross section through a simple sphalerite twin showing the different "two dimensional" hexagonal crystal unit cells that exist at the twin boundary. Only the Zn (or S) atoms are designated.

edges formed by the intersections of tetrahedral faces. This is the same orientation the wurtzite had in relationship to the sphalerite (111) faces. The similarity between the axial ratios of hexagonal zinc oxide and zinc sulfide also show how closely these structures are related: $\text{ZnO } a:c=1:1.608$; $\text{ZnS, } a:c=1:1.635$ (after Bragg, 1920).

Silicon carbide possesses a twinning property somewhat similar to that of the isostructural zinc sulfide. Cubic crystals have been observed by Thibault (1944) which contain thin plates of α silicon carbide parallel to adjacent faces of the positive and negative tetrahedrons. These plates are inclined to one another $70^\circ 32'$ which is the octahedral angle. This is the same angle at which the wurtzite prisms in Figs. 2, 3a, and 4 are inclined to each other. If two of these plates of α silicon carbide continued to grow until their size completely hid the cubic section, one would observe a twinning arrangement of them in which the basal pinacoids of

the individuals are inclined to each other at an angle of $70^{\circ} 32'$. Numerous examples of silicon carbide twins have been observed with angles approaching this value (Thibault, 1944; Padurow, 1952). Thibault has suggested that this twinning angle is related to the octahedral angle in the manner described above. However, he suggests that the cubic section has reverted to hexagonal silicon carbide at an elevated temperature. From our knowledge of the coexistence of the zinc sulfide forms, the writers feel that with more investigation it may be proven that the cubic modification still exists at the "twinning" boundary.

Slawson and Kohn (1950) have pointed out that diamond, which is isostructural with sphalerite, may possibly have a hexagonal modification similar to the structure of wurtzite. They have pointed out that it would have a low double refraction, a density of approximately 3.50, and a hardness nearly equal to that of the cubic modification. In a sense this modification actually exists as a "two dimensional" crystal at the twinning boundary in a spinel twin of diamond (the same situation discussed earlier for twinned sphalerite, Fig. 8). This hexagonal modification is one unit cell high in the direction of its c axis (diamond [111]) and in the other two directions, extends to the bounds of the crystal. It can be considered $2H$, $4H$, $6H$, \dots , $2nH$ (see footnote, page 780). Slawson and Kohn (1950) have suggested that the anomalous double refraction in diamond may be due to the presence of many of these hexagonal levels caused by repeated twinning in the diamond. A real three dimensional modification would not exist, however, unless the twinning occurred by rotating every other layer of atoms in diamond 180° around the diamond [111] axis. The study of diamond flats (crystals flattened along (111)) showing double refraction should eventually result in the identification of this predicted form.

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